**Identification of lithium-sulfur battery discharge products through ^6Li and ^{33}S solid-state
MAS and ^7Li solution NMR spectroscopy**

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Abstract

^6Li and ^{33}S solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy were used to identify the discharge products in lithium-sulfur (Li-S) battery cathodes. Cathodes were stopped at different potentials throughout battery discharge and measured *ex-situ* to obtain chemical shifts and T_2 relaxation times of the products formed. The chemical shifts in the spectra of both ^6Li and ^{33}S NMR demonstrate that long-chain, soluble lithium polysulfide species formed at the beginning of discharge are indistinguishable from each other (similar chemical shifts), while short-chain, insoluble polysulfide species that form at the end of discharge (presumably Li_2S_2 and Li_2S) have a different chemical shift, thus distinguishing them from the soluble long-chain products. T_2 relaxation measurements of discharged cathodes were also performed which resulted in two groupings of T_2 times that follow a trend and support the previous conclusions that long-chain polysulfide species are converted to shorter chain species during discharge. Through the complementary techniques of 1-D ^6Li and ^{33}S solid-state MAS NMR spectroscopy, solution ^7Li and ^1H NMR spectroscopy, and T_2 measurements, structural information about the discharge products of Li-S batteries is obtained.

1. Introduction

New energy storage devices and battery chemistries are needed to meet the increasing energy storage demands of the future, which must be suited to store power for electric vehicles, renewable energies, and the grid, due to the increasingly pressing need to sustain the

environment.[1] The now ubiquitous lithium-ion (Li-ion) battery revolutionized the battery industry when it was first commercialized by Sony in 1991 by demonstrating exceptionally high potential, high energy density, low self-discharge rate, and long cycle life.[2] The Li-ion battery quickly dominated many portable electronic devices including phones, camcorders, laptop computers, among others.[2, 3] However, despite the many advantages of the Li-ion battery, there are many disadvantages. These include: safety concerns, scarcity of battery constituents such as Co, and insufficient capacity for demanding uses such as transportation.[2-6]

One of the leading next-generation energy storage candidates to replace the Li-ion battery is the Li-S battery.[4] The Li-S battery features several attractive advantages over other types of batteries. These advantages include: a substantially higher theoretical energy density relative to conventional insertion Li-ion cathodes (2600 Wh kg^{-1} versus 800 Wh kg^{-1} , respectively),[7] a high specific capacity of 1675 mAh g^{-1} (calculated based on sulfur)[4], as well as the high natural abundance and low cost of sulfur, the cathode active material.[4, 8] The Li-S battery contains a lithium metal anode (negative electrode) and a mixed carbon/sulfur cathode (positive electrode). During discharge, lithium ions travel from the anode, through a separator (Li-ion-selective) and on to the cathode where they react with elemental sulfur (S_8), cleaving S-S bonds in the eight-membered sulfur rings and forming lithium polysulfide products (Li_2S_n , where $n \leq 8$). Ultimately Li_2S is the desired discharge product, which is stored on the cathode as a solid deposit until the battery is recharged, whereupon the Li_2S reversibly re-forms longer chain lithium polysulfide species. The discharge curve consists of three characteristic plateau regions (shown in Figure 1), which indicate three different reaction processes that occur during discharge. Evidence for the presence of different polysulfide chain lengths at different potentials of the battery discharge is abundant in the literature.[7, 9, 10]

Despite the major advantages that the Li-S battery offers and decades of research, a Li-S battery with longer cycle life and sufficient energy storage to meet future transportation requirements has not yet been realized.[4] Problems with the battery chemistry include: (1) low rechargeability, low discharge/charge rates[11] due to the insulating properties of elemental sulfur (S_8) and the solid discharge products Li_2S and Li_2S_2 , (2) low cycle life due to the well-established lithium polysulfide shuttle mechanism whereby soluble polysulfide species migrate between the anode and cathode,[12] and (3) poor electrolyte solvent options.[4] The problem of lithium polysulfide dissolution has been partially resolved in previous reports through encapsulation of the sulfur active material at the cathode using various carbon hosts including mesoporous carbon spheres,[1, 13, 14] carbon nanofibers,[15-17] carbon fiber,[18] and graphene oxides,[19] and non-carbon hosts such as TiO_2 yolk-shell nanospheres.[20]

However, incomplete knowledge of the discharge products formed during battery cycling and the Li/electrolyte interface inhibits efficient design of the Li-S cell chemistry. Understanding speciation in different potential regions as the battery is discharged will provide insight into the discharge mechanism. The knowledge of the mechanism of various reactions will help in the design of cathodes which minimize polysulfide formation and promote the formation of Li_2S .

Prior studies have used various techniques to identify discharge products in Li-S battery cathodes including XRD,[21-23] UV-vis spectroscopy,[9, 24] Raman spectroscopy,[23] XPS,[1, 25] FTIR,[26] EPR,[9] and X-ray studies (XANES).[27] Relatively little work attends to the investigation of Li-S batteries using nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy is a powerful technique to apply to batteries, as demonstrated by the many investigations into Li-ion systems by Li NMR.[28-33] We are aware of only one other paper

that investigated Li-S battery products through Li MAS NMR spectroscopy.[27] This previous study utilized synthesized lithium polysulfide species as references for XANES S k-edge studies of Li-S battery products and characterized the prepared references (Li_2S , Li_2S_2 , Li_2S_6 , and a two-component model for Li_2S_8) using XRD and ^7Li MAS NMR spectroscopy. This study concluded that only two distinct Li environments exist for Li_2S and Li_2S_6 (at 2.3 and 1.0 ppm, respectively). This previous investigation used a different isotope of lithium (^7Li) than our study (^6Li), however it is noteworthy that chemical shift values are nominally the same between the two isotopes.[34]

In this paper, we use ^6Li and ^{33}S magic angle spinning (MAS) and solution ^7Li and ^1H NMR spectroscopy methods to examine discharge products from Li-S battery cathodes. In addition to chemical shift information, we find that relaxation times (T_2 in particular) provide a powerful analytical method to distinguish between lithium polysulfide products in the battery.

2. Materials and Methods

Lithium-sulfur batteries were assembled inside a modified Swagelok tube fitting apparatus (nylon, $\frac{1}{2}$ " inner diameter, purchased from Chicago Fluid System Technologies) inside an argon-filled glove box (<2 ppm O_2). The battery components were layered inside the tube fittings, between two solid stainless steel cylinders that serve as electrical connections, in the following order: lithium metal foil (as the anode, 0.75×45 mm thickness, 99.9% trace metals basis, Sigma-Aldrich), Celgard 2400 (polypropylene separator), Whatman glass fiber, (GF/F, 150mm diameter, separator), and Li-S cathode slurry coated onto aluminum foil (Sigma-Aldrich). The electrolyte was 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1:1

tetraethylene glycol dimethyl ether (TEGDME, $\geq 99\%$, Sigma-Aldrich)/1,3-dioxolane (DIOX or DOL, anhydrous, ~ 75 ppm BHT as inhibitor, Sigma-Aldrich).

The Li-S cathode slurry consists of carbon black (2.14 wt. %, Super P Li, Timcal), polyvinylidene fluoride (PVDF) (0.71 wt. %, Kynar 2801), sulfur (4.29 wt. %, Sigma-Aldrich) and 1-methyl-2-pyrrolidone (NMP) (92.86 wt. %, TCI). The slurry components were stirred for 12 hours, cast on to aluminum foil (Sigma-Aldrich) with a thickness of 12 μm using a Gardco adjustable micrometer film applicator (Microm II, 5 $\frac{1}{2}$ " width), then allowed to dry at 55°C for 24 h. The Li-S cathode slurry + aluminum foil was then cycled into a glove box and punched into 1"-diameter circles for use as cathodes.

Li-S battery discharge

Electrochemical discharge of the batteries was performed on model 760C and 760D CHI instruments electrochemical workstations using chronopotentiometry. Batteries were cycled at a rate of C/60 (by weight of the whole cathode) or C/2.6 (by weight of sulfur in cathode only) from the open circuit potential (OCP) to the desired cut-off potentials of 2.15, 2.03, and 1.50 V (vs. Li/Li⁺). All batteries were cycled and disassembled inside an argon-filled glove box (< 2 ppm O₂).

⁶Li NMR spectroscopy

⁶Li DPMAS (direct-polarization magic angle spinning) NMR spectroscopy, T₁ and T₂ experiments were performed on a 7.1 T Varian Unity Inova 300 (Varian is now part of Agilent Technologies) spectrometer, equipped with a 4 mm Varian Chemagnetics APEX Double

Resonance HX probe. The cathode and powder samples were packed in silicon nitride rotors inside a glove box, sealed, then removed from the glove box and spun to 10 kHz inside the spectrometer. ^6Li MAS NMR spectra were then acquired *ex-situ* in sealed rotors for each of the cathodes discharged to the three characteristic plateau regions (i.e. at 2.15, 2.03, and 1.50 V). A ^6Li MAS NMR spectrum was also acquired for dry Li_2S powder (dried under vacuum overnight on the Schlenk line). Electrolyte solution (1 M LiTFSI in 1:1 TEGDME/DIOX) was added to an un-cycled Li-S cathode and the cathode + electrolyte sample was packed into a solid-state NMR rotor to determine whether the carbon cathode caused any changes in the electrolyte salt (LiTFSI) environment that would alter its chemical shift. The solution electrolyte (1 M LiTFSI in 1:1 TEGDME/DIOX) was pipetted into a small glass NMR tube and NMR spectra were acquired in the same solid-state probe used for the cathode and powder samples. The ^6Li chemical shifts were referenced to a 1 M LiCl solution at 0 ppm. T_2 relaxation measurements were conducted using a Hahn-Echo pulse sequence. All ^6Li MAS NMR experiments employed a magic angle spinning speed of 10 kHz. A recycle delay of 7200 s was used for all T_2 relaxation experiments. Additional experimental parameters for ^6Li MAS NMR are given in the figure captions, employing the following symbols: B_0 (magnetic field strength), ν_r (magic angle spinning rate), d_1 (relaxation delay), nt (number of transients), and lb (line broadening). T_2 relaxation times were determined through fitting to a mono-exponential equation in MestReNova (MNova) to determine M_0 (Equation 1) and by plotting the natural log of peak height versus τ in OriginPro 8.6. T_2 relaxation time is taken as the negative inverse of the slope and the error in T_2 is determined through residual analysis of the slope in the natural logarithm plot.

Solution ^7Li and ^1H NMR spectroscopy

Li-S battery cathodes that were discharged in the glove box were dried under vacuum in the glove box for 12 h. The cathodes were then soaked in 1:1 TEGDME/DIOX solvent for 1 h, during which time the solution would change color from clear to yellow-orange at the beginning of discharge (~2.15 V) or teal to dark green toward the end of discharge (~2.03-1.5 V). The solution was then transferred to a clean solution NMR tube. A small amount (0.2 mL) of deuterated acetonitrile (CD_3CN) was added to the first sample on a Schlenk line to obtain a solvent lock on the spectrometer, however all subsequent samples contained no deuterated solvent. Solution NMR measurements were referenced to a 1 M solution of LiCl (to 0 ppm) and performed on a 14.1 T spectrometer.

Solid-state ^{33}S MAS NMR spectroscopy

Discharged Li-S battery cathodes and dry Li_2S powder were packed into 5-mm pencil solid-state rotors in a glove box and sealed. Rotors were transported to the Chemistry Department of the University of Akron for all ^{33}S solid-state MAS NMR measurements. All experiments were performed on a 17.6 T (750 MHz for ^1H) Agilent Direct-Drive 2 spectrometer, which was equipped with a Varian/Chemagnetics T3 double-channel probe, optimized for observing ^{33}S . All ^{33}S MAS NMR samples were spun to 11 kHz and the chemical shifts were referenced to -29.0 ppm with CaS powder. The ^{33}S MAS NMR parameters used were as follows: the calibrated 90-degree pulse was 9.5 μs (26 MHz) but a 20-degree pulse of 2.1 μs was used, the spectral width was 100 kHz, acquisition time (at) was 0.1 s, recycle delay was 3.0 s, zero filling (fn) was 65536, and number of transients (nt) was 12800 for the cathode discharged to 1.5 V and 4096 for the Li_2S powder. A ^1H decoupling field of 11.6 kHz was used. Additionally, backward linear prediction was applied to the first three points of both spectra using a linear coefficient of 32 and a basis set of 256 points. Additional experimental parameters for

^{33}S MAS NMR are given in the figure captions, employing the following symbols: nt (number of transients) and lb (line broadening).

3. Results

Figure 1 shows a typical discharge curve obtained from a Li-S battery[9]. The discharge curve shown in Figure 1 is a typical result obtained from a Li-S battery discharged at a rate of $\text{C}/2.6$ (or 0.4C), with a typical capacity of approximately $930 \text{ mAh g}^{-1}_{\text{whole cathode}}$ or $1550 \text{ mAh g}^{-1}_{\text{sulfur}}$. This capacity is similar to that reported previously by several groups, with capacities ranging from $800\text{-}1200 \text{ mAh g}^{-1}_{\text{sulfur}}$ at equivalent discharge rates.[25] The Li-S battery discharge curve typically consists of three plateau regions (labeled in Figure 1): two main plateau regions (Reg. 1 and 3), and a smaller region (Reg. 2) that occurs just after Region 1 and appears as a small shoulder in the discharge curve. Region 1 is associated with S_6^{2-} and S_3^{2-} as evidenced by UV-vis spectroscopy conducted in previous studies[9]. The second plateau region is less distinguishable than regions 1 and 3, however it is associated with S_4^{2-} . Region 3 is associated with S_3^{2-} , S_2^{2-} and S^{2-} . [9, 25]

Figure 1: A Li-S battery discharge curve (chronopotentiometric) at a C/2.6 rate (C/60 for weight of whole cathode).

Of particular interest in this study was whether the components present in the cathodes discharged to each of the three regions of discharge observed in the discharge curve (Figure 1) could be identified using NMR spectroscopy. Figure 2 shows ^6Li solid-state MAS NMR obtained from several different control samples. The LiTFSI powder, the solution electrolyte, which consists of 1 M LiTFSI in 1:1 TEGDME/DIOX, and the un-cycled cathode with solution electrolyte all exhibit a single peak that ranges from -1.46 to -1.22 ppm relative to LiCl. Shifts similar to these have previously been reported[35, 36][36, 37]. ^6Li NMR resonances that occur between ± 10 ppm are attributed to lithium ions in diamagnetic environments, including battery electrolyte solutions and the solid electrolyte interface (SEI) of lithium-ion batteries.[35] Resonances from ^6Li located in paramagnetic environments are shifted by as much as -500 to

+3,000 ppm due to hyperfine interactions with paramagnetic materials. Metallic lithium has a ^6Li chemical shift of 250 ppm due to interactions with electrons in the conduction band of the metal, referred to as Knight shift interactions.[35]

Fig. 2 also shows the ^6Li MAS NMR obtained from a sample of dry Li_2S powder. In contrast to the other three spectra, the single peak seen here is at 2.40 ppm, located significantly downfield from the LiTFSI resonance. This downfield shift indicates that the lithium nucleus is more de-shielded than it is in the presence of the Cl^- environment from the LiCl reference compound. Additionally, this chemical shift (2.40 ppm) for Li_2S is extremely close to that observed previously for Li_2O at 2.87 ppm[38]. Li_2S and Li_2O exhibit similar chemical shifts because sulfur and oxygen have similar electron-withdrawing and bonding properties. The chemical shift of Li_2S is located slightly upfield from that of Li_2O since sulfur is less electronegative than oxygen and therefore has weaker electron-withdrawing properties, resulting in more shielded lithium nuclei in the Li_2S powder.

Figure 2: ${}^6\text{Li}$ solid-state MAS NMR spectra of (a) electrolyte salt LiTFSI powder, (b) the solution electrolyte (1 M LiTFSI in 1:1 TEGDME/DIOX), (c) an uncycled cathode containing electrolyte solution, and (d) dry Li_2S powder. $B_0 = 7.1$ T, $\nu_r = 10$ kHz.

Figure 3 shows the MAS ${}^6\text{Li}$ NMR spectra obtained from cathodes containing 1 M LiTFSI in 1:1 TEGDME/DIOX electrolyte discharged to 2.15, 2.03, and 2.00 V. These cathodes, discharged to regions 1 and 2 of the discharge curve, all exhibit very similar chemical shifts (-0.53, -0.29 and -0.76 ppm, respectively). These shifts are located downfield relative to the electrolyte standards shown in Fig 2, suggesting that the lithium products formed in the first two regions of battery discharge contain lithium nuclei that are more de-shielded than those in

the LiTFSI electrolyte salt. In other words, the lithium nuclei in the battery products formed in the first two potential regions are in a less electron-rich environment.

Figure 3 also shows the ^6Li MAS NMR spectra obtained from a cathode discharged to 1.50 V. In contrast to the results obtained at the previous three discharge voltages, the discharge products in batteries discharged fully to 1.50 V exhibit two peaks at 2.32 and 0.12 ppm. The peak at 2.32 ppm has a chemical shift that is very similar to that found for Li_2S in Fig. 2 at 2.40 ppm. However, the peak at 0.12 ppm is not found in the standards reported above. The 0.12 ppm shift is similar to the 0.11 ppm shift found previously for Li_2CO_3 , and it is possible that a small amount of carbon in the Li-S battery cathode is oxidized to Li_2CO_3 at the end of battery discharge[38].

Figure 3: ^6Li solid-state MAS NMR spectra of Li-S battery cathodes discharged to (a) 2.15 V, (b) 2.03 V, (c) 2.00 V, and (d) 1.50 V. $B_0 = 7.1$ T, $\nu_r = 10$ kHz.

In order to provide further discrimination between discharge products, we measured the T_2 times associated with each peak. The T_2 decay time for each cathode was determined using the Hahn-echo pulse (90° and 180° pulses) technique, where spectra were acquired for an arrayed set of times between the pulses (τ). The resulting peak heights were then fit to the mono-exponential curve,

$$M_y(2\tau) = M_0 \exp(-2\tau/T_2)$$

(1)

where M_y is the amplitude of the transverse magnetization (proportional to peak height), M_0 is the amplitude of the magnetization just before an applied pulse, and τ is the arrayed delay time between the two Hahn echo pulses.[39] The resulting peak heights are plotted against τ and fit to the above mono-exponential fit (Equation 1) for each of the cathodes discharged to different potentials (2.15, 2.03 and 1.50 V). Cathodes discharged to different potentials exhibit different slopes in the plot of peak height versus τ values, where the cathode discharged to the furthest depth of discharge (1.50 V) results in the highest decay rate and the cathodes discharged to smaller depths of discharge (2.03 and 2.15 V) result in smaller decay rates.

Table 1 shows measured T_2 relaxation times for cathodes discharged to 2.15, 2.03 and 1.50 V and Li_2S powder using ^6Li solid-state MAS NMR spectroscopy. The T_2 times for the products formed in the Li-S battery cathodes follow a trend where the T_2 time is smaller for the cathode discharged to a lower potential (i.e. discharged to a greater extent, to 1.50 V) and larger for the two cathodes discharged to a higher potential (i.e. 2.03 and 2.15 V). The T_2 time for the Li_2S powder does not exactly match that of any of the measured discharged cathodes, and is smaller than any T_2 values obtained for the cathodes.

	NMR chemical shift	Measured	Error in
	(ppm)	T_2 (ms)	T_2 (ms)
Cathode to 2.15 V	-0.78	49	± 5
Cathode to 2.03 V	-1.25	41	± 4
Cathode to 1.50 V	2.25	26.5	± 0.6
Li_2S powder	2.35	11.9	± 0.5

Table 1: Experimentally measured T_2 relaxation times for Li-S battery cathodes discharged to 2.15, 2.03, 1.50 V, and dry Li_2S powder through solid-state ^6Li MAS NMR spectroscopy with standard error reported. $B_0 = 7.1$ T, $\nu_r = 10$ kHz.

Preliminary T_1 relaxation time measurements were found to require excessive measurement times (ca. 4 days per measurement) and were not continued.

Table 2 shows solution ^1H and ^7Li NMR spectroscopy data of products extracted from cathodes discharged to different potential regions and a standard electrolyte solution. The ^7Li solution NMR chemical shifts for all products extracted from cathodes discharged to 2.40, 2.03 and 1.98 V were very similar, in the range of -1.27 to -1.35 ppm. The ^7Li NMR chemical shift for solution LiTFSI is very different than that of the Li-S battery discharge products, similar to the results from solid state ^6Li MAS NMR, at -2.39 ppm.

Species	^7Li chemical shift (ppm)	^1H chemical shift (ppm)
2.40 V	-1.29	4.08, 3.86, 3.78, 3.60, 2.70, 2.59, 2.35, 2.24, 2.12
2.03 V	-1.35	4.11, 3.90, 3.81, 3.64, 2.73, 2.39, 2.28, 2.16
1.98 V	-1.27	3.99, 3.78, 3.70, 3.52, 2.61, 2.27, 2.16, 2.04
LiTFSI (in CH_3CN)	-2.39	--

Table 2: Solution ^7Li and ^1H NMR data of products extracted from Li-S cathodes discharged to different potentials (2.40, 2.03 and 1.98 V) in non-deuterated acetonitrile, LiTFSI in CH_3CN , and aqueous 1 M LiCl. $B_0 = 14.1$ T.

Figure 4 shows the solid-state ^{33}S MAS NMR spectra of cathode material removed from a Li-S battery discharged to 1.50 V and standard Li_2S powder, which resulted in clear, sharp ^{33}S NMR peaks. The chemical shifts for the cathode discharged to 1.50 V and Li_2S powder are extremely similar (at -344.1 and -342.7 ppm, respectively). The ^{33}S NMR peak for the cathode (discharged to 1.50 V) is broader and shifted slightly upfield compared to the NMR peak for Li_2S powder, which is extremely sharp and slightly downfield. The broadness of the ^{33}S NMR peak for the discharged cathodes is attributed to the presence of different lithium polysulfide species that may not have all been converted to the final Li_2S product. Longer-chain polysulfides such as Li_2S_2 , Li_2S_4 , Li_2S_6 , etc. could still be present in the cathode in small amounts particularly since these measurements were conducted *ex-situ* and it is possible that chemical reactions (such as disproportionation reactions) may occur after the battery discharge is stopped and the cathode is no longer held at a certain potential.

Spectra obtained from cathodes discharged to other potentials, however, did not exhibit clear peaks and showed only rolling baselines. A rolling baseline, attributed to “acoustic ringing,” is a well-known phenomenon that occurs in NMR probes used at low frequencies[40, 41]. The baseline results from a physical resonance frequency inside the NMR probe causing a ring-down phenomenon to occur inside the probe, distorting the first few points in the NMR free

induction decay (FID) and yielding a large, moving, rolling baseline in the resulting NMR spectra[40].

An additional complication in studying elemental sulfur or polysulfides is the breadth of the NMR peak which has been reported at ± 500 ppm[42]. In one particularly clear spectrum of elemental sulfur powder, we found a peak ranging from +800 to -700 ppm centered at around -50 ppm. This sulfur peak does appear in other spectra from discharged cathodes acquired as either a shoulder on a rolling baseline or a small peak, but the background noise is too large to conclusively determine whether or not this feature obtained for sulfur powder is real. Therefore, information about the soluble lithium polysulfide species was not obtained in the ^{33}S MAS NMR studies.

Figure 4: Solid-state ^{33}S MAS NMR spectra of (a) a Li-S battery cathode discharged to 1.5 V and (b) dry Li_2S powder. $B_0 = 17.6$ T, $\nu_r = 11$ kHz, line broadening = 200 Hz.

4. Discussion

The discharge curve shown in Figure 1 exhibits the three characteristic plateau regions that are associated with three different reaction processes[9, 23]. The identity of these processes is still controversial and may include S-S bond cleavage by lithium ions, disproportionation reactions, and differing degrees of polysulfide, Li_2S_2 , and Li_2S formation[4]. In this work we use ^6Li and ^{33}S solid-state MAS NMR spectroscopy (with both 1-D and T_2 relaxation measurements) to investigate the products formed in each of the three characteristic plateau regions in order to further elucidate the discharge reaction mechanisms.

The consistent ^6Li NMR chemical shift observed for LiTFSI, regardless of differing chemical environments tested demonstrates that the electrolyte salt is insensitive to the surrounding chemical environments and additionally that the LiTFSI salt has a different chemical shift than the Li_2S powder (Figure 2). Powders of other chain lengths of lithium polysulfides are not available for use as standards. LiTFSI is not found in discharged cathodes, which means that solvent incorporation in the cathode (following addition of electrolyte) is minimal. This background study confirms that the LiTFSI salt, which is the only other source of lithium in the battery aside from the anode, does not interfere with identification of the final discharge products.

^6Li solid-state MAS NMR chemical shift measurements (Figure 3) of discharged Li-S cathodes and Li_2S powder demonstrate that cathodes discharged to 2.15, 2.03, and 2.00 V exhibit

very similar chemical shifts. Because these different voltage plateaus are associated with terminal Li polysulfide species of different lengths, it is suggested that changes in the number of neighboring sulfur atoms do not affect the electronic environment of the terminal lithium atoms strongly enough to further de-shielded them. The slight variation in chemical shift observed may be a consequence of disproportionation reactions from the highly soluble polysulfides[4, 9, 23] continuing after battery discharge is terminated. Thus, products of these disproportionation reactions may contribute to the observed signals. There is likely a distribution of different lithium polysulfide species present in the Li-S battery at each potential throughout discharge due to mass transport and kinetic limitations, as well as on-going disproportionation reactions and the well-known polysulfide shuttle mechanism[4, 7]. This means that there are a number of lithium polysulfide chain lengths present in each cathode contributing to the aggregate observed chemical shift.

Cathodes discharged to the final voltage of 1.50 V have the same ^6Li MAS NMR chemical shift as Li_2S powder. The slight (0.08 ppm) difference between the chemical shifts of the cathode discharged to 1.50 V and the Li_2S powder may be due to small, additional contributions from other Li polysulfide species (such as solid Li_2S_2).

It is clear from the ^6Li solid-state MAS NMR studies that chemical shift alone does not allow the different chain lengths of lithium polysulfide species other than Li_2S to be distinguished. T_2 (spin-spin or transverse) relaxation measurements were conducted as a complementary method to distinguish the different polysulfide chain lengths since it is known that T_2 relaxation is affected by molecular size and physical state[43]. T_2 relaxation was chosen rather than T_1 (spin-lattice or longitudinal) relaxation because $T_2 \leq T_1$ for solid-state species and therefore the measurement time is shorter. T_2 relaxation is caused by de-coherence of the

magnetization of the nuclei under observation in the transverse plane (i.e. the plane perpendicular to the direction of the applied external magnetic field), which is due only to inhomogeneous interactions of the surrounding environment with the excited-state nuclei.

Two different groupings of T_2 relaxation times were measured for Li-S cathodes discharged to the ends of the three potential regions, indicating T_2 relaxation measurements may be a useful tool to distinguish products formed during the Li-S battery discharge. While it appears from the measured T_2 relaxation times that the cathodes discharged to 2.03 and 2.15 V yield different T_2 relaxation times, the error associated with these measurements due to low signal-to-noise of the ^6Li MAS NMR spectra indicates that the difference in T_2 relaxation times determined for cathodes discharged to 2.03 and 2.15 V are not statistically significant. Further studies with ^6Li -labeled samples or longer collection times would be needed to determine whether or not the T_2 relaxation times are distinguishable for cathodes discharged to smaller depths of discharge (i.e. 2.03 and 2.15 V).

The two groups of measured T_2 relaxation values follow a trend associated with the extent of cathode discharge, where the products in cathodes discharged to more negative potentials have smaller T_2 times. T_2 relaxation times are affected by several different factors, which are related to the correlation time (τ_c , related to Brownian motion) of the species under investigation. These factors include: (1) molecular size, where smaller T_2 values generally indicate larger molecular size, (2) viscosity, where smaller T_2 relaxation times indicate higher viscosity (decreased molecular movement),^[43] and (3) temperature, where lower temperatures cause T_2 relaxation times to decrease.^[44] These parameters are related by the equation below (Equation 2), which is derived from the Stokes' law with a spherical approximation.

$$\tau_c = \frac{4\pi\eta r^3}{3kT} \quad (\text{Equation 2})$$

Where η is viscosity of the solvent, r is the radius of the molecule, k is the Boltzmann constant, and T is the temperature.[44] In the present system, temperature is constant and thus cannot contribute to the observed T_2 relaxation time changes. Possible viscosity changes in the electrodes discharged to different potentials could be associated with changes in the Solid Electrolyte Interphase (SEI) that may occur at different degrees of discharge. Little is understood presently about the SEI formed on the cathode aside from insulating elemental sulfur and solid product deposits such as Li_2S_2 and Li_2S .[45] The anode SEI is known to contain lithium polysulfide species along with solvent degradation products where lithium polysulfide species (Li_2S_n) may react with the ether-based solvents (R-O-R) to form R-OLi and R- Li_2S_n species.[46]

The final possibility for changes in T_2 relaxation times with degree of discharge relates to the different molecular sizes of discharge products formed. In particular, at low discharge potentials, higher molecular weight polysulfides are present, while at high discharge potentials, Li_2S has been demonstrated previously to be the major product formed. We therefore assign differences in T_2 relaxation times at different depths of discharge to different sizes of lithium polysulfide products in the battery cathodes, where smaller polysulfides are found at lower potentials, consistent with prior results.[9]

The solid Li_2S powder has a different T_2 relaxation time than that of the products formed in the fully discharged (1.50 V) cathode (11.9 and 26 ms, respectively, Table 1). The origin of the increased relaxation time is likely the presence of species in addition to Li_2S in the discharged cathode. In particular, the ^6Li NMR spectrum of cathodes discharged to 1.50 V

results in two peaks: one attributed to Li_2S and one attributed to an oxide species such as Li_2CO_3 (2.32 and 0.12 ppm, respectively). Additionally, the Li_2S powder is crystalline while the products formed in the fully discharged cathode may be amorphous or only have short-range crystalline order, the differences of which also contribute to chemical shift dispersion[47].

Like the ^6Li MAS, solution ^7Li NMR of electrolyte solution and extracted products from discharged Li-S battery cathodes (Table 2) also exhibits minimal chemical shift differences among cathodes discharged between 2.15 V and 2.00 V. Since chemical shift differences between ^6Li and ^7Li NMR spectra are not significant[34], chemical shifts between the two isotopes may be directly compared. Spectra obtained from solutions above cathodes discharged to 1.5 V did not exhibit a signal attributable to the discharge product, likely a consequence of Li_2S insolubility. The ^1H spectra acquired for all of the extracted products from discharged Li-S batteries have been attributed to the TEGDME/DIOX solvent present in the cathodes.

Solid-state ^{33}S MAS NMR of cathodes discharged to 1.50 V and Li_2S powder (Figure 4) also suggests that the cathodes discharged to this potential contain mostly Li_2S . The increased width of the ^{33}S NMR peak for the discharged cathode relative to that of Li_2S powder suggests again that the cathode likely contains a small amount of other lithium polysulfide species contributing to its line shape.

5. Conclusions

^6Li T_2 relaxation measurements show that the first two characteristic plateau regions present in Li-S battery discharge curves are associated with larger lithium polysulfide species (at 2.03 and 2.15 V) that react to form smaller lithium polysulfide species with further depth of

discharge into the third plateau region (at 1.50 V). Additionally, both solid-state ^6Li and ^{33}S MAS NMR studies demonstrate that Li_2S is produced only at the end of the Li-S battery discharge in cathodes discharged to 1.50 V, along with small amounts of longer-chain lithium polysulfide species. ^6Li , ^{33}S MAS NMR, and ^6Li T_2 relaxation measurements all resulted in two regions of product formation during discharge, where the first state of discharge occurs in the first two plateau regions and the second state of discharge occurs in the third plateau region. These studies indicate that NMR spectroscopy is a powerful tool to study differences between the solution and solid-state products (i.e. soluble long-chain Li polysulfide species and insoluble Li_2S_2 and Li_2S , respectively). Additionally T_2 relaxation measurements may be useful to distinguish between Li polysulfide products in all three states of discharge with further studies.

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References

- [1] J. Kim, D.-J. Lee, H.-G. Jung, Y.-K. Sun, J. Hassoun, B. Scrosati, An Advanced Lithium-Sulfur Battery, *Advanced Functional Materials*, 23 (2013) 1076-1080.

- [2] M. Armand, J.M. Tarascon, Building better batteries, *Nature*, 451 (2008) 652-657.
- [3] P.G. Bruce, B. Scrosati, J.-M. Tarascon, Nanomaterials for Rechargeable Lithium Batteries, *Angewandte Chemie International Edition*, 47 (2008) 2930-2946.
- [4] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, Li-O₂ and Li-S batteries with high energy storage, *Nat Mater*, 11 (2012) 19-29.
- [5] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature*, 414 (2001) 359-367.
- [6] P.G. Bruce, Energy storage beyond the horizon: Rechargeable lithium batteries, *Solid State Ionics*, 179 (2008) 752-760.
- [7] A. Manthiram, Y. Fu, Y.-S. Su, Challenges and Prospects of Lithium–Sulfur Batteries, *Accounts of Chemical Research*, 46 (2012) 1125-1134.
- [8] X. Ji, L.F. Nazar, Advances in Li-S batteries, *Journal of Materials Chemistry*, 20 (2010) 9821-9826.
- [9] C. Barchasz, F. Molton, C. Duboc, J.-C. Leprêtre, S. Patoux, F. Alloin, Lithium/Sulfur Cell Discharge Mechanism: An Original Approach for Intermediate Species Identification, *Analytical Chemistry*, 84 (2012) 3973-3980.
- [10] R.D. Rauh, K.M. Abraham, G.F. Pearson, J.K. Surprenant, S.B. Brummer, A Lithium/Dissolved Sulfur Battery with an Organic Electrolyte, *Journal of The Electrochemical Society*, 126 (1979) 523-527.
- [11] Y.-J. Choi, K.-W. Kim, H.-J. Ahn, J.-H. Ahn, Improvement of cycle property of sulfur electrode for lithium/sulfur battery, *Journal of Alloys and Compounds*, 449 (2008) 313-316.
- [12] Y.V. Mikhaylik, J.R. Akridge, Polysulfide Shuttle Study in the Li/S Battery System, *Journal of The Electrochemical Society*, 151 (2004) A1969-A1976.

- [13] X. Ji, K.T. Lee, L.F. Nazar, A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries, *Nat Mater*, 8 (2009) 500-506.
- [14] N. Jayaprakash, J. Shen, S.S. Moganty, A. Corona, L.A. Archer, Porous Hollow Carbon@Sulfur Composites for High-Power Lithium–Sulfur Batteries, *Angewandte Chemie International Edition*, 50 (2011) 5904-5908.
- [15] G. Zheng, Y. Yang, J.J. Cha, S.S. Hong, Y. Cui, Hollow Carbon Nanofiber-Encapsulated Sulfur Cathodes for High Specific Capacity Rechargeable Lithium Batteries, *Nano Letters*, 11 (2011) 4462-4467.
- [16] J. Guo, Y. Xu, C. Wang, Sulfur-Impregnated Disordered Carbon Nanotubes Cathode for Lithium–Sulfur Batteries, *Nano Letters*, 11 (2011) 4288-4294.
- [17] L. Ji, M. Rao, S. Aloni, L. Wang, E.J. Cairns, Y. Zhang, Porous carbon nanofiber-sulfur composite electrodes for lithium/sulfur cells, *Energy & Environmental Science*, 4 (2011) 5053-5059.
- [18] R. Elazari, G. Salitra, A. Garsuch, A. Panchenko, D. Aurbach, Sulfur-Impregnated Activated Carbon Fiber Cloth as a Binder-Free Cathode for Rechargeable Li-S Batteries, *Advanced Materials*, 23 (2011) 5641-5644.
- [19] L. Ji, M. Rao, H. Zheng, L. Zhang, Y. Li, W. Duan, J. Guo, E.J. Cairns, Y. Zhang, Graphene Oxide as a Sulfur Immobilizer in High Performance Lithium/Sulfur Cells, *Journal of the American Chemical Society*, 133 (2011) 18522-18525.
- [20] Z. Wei Seh, W. Li, J.J. Cha, G. Zheng, Y. Yang, M.T. McDowell, P.-C. Hsu, Y. Cui, Sulphur–TiO₂ yolk–shell nanoarchitecture with internal void space for long-cycle lithium–sulphur batteries, *Nat Commun*, 4 (2013) 1331.

- [21] S. Walus, C. Barchasz, J.-F. Colin, J.-F. Martin, E. Elkaim, J.-C. Lepretre, F. Alloin, New insight into the working mechanism of lithium-sulfur batteries: in situ and operando X-ray diffraction characterization, *Chemical Communications*, 49 (2013) 7899-7901.
- [22] N.A. Cañas, S. Wolf, N. Wagner, K.A. Friedrich, In-situ X-ray diffraction studies of lithium-sulfur batteries, *Journal of Power Sources*, 226 (2013) 313-319.
- [23] J.-T. Yeon, J.-Y. Jang, J.-G. Han, J. Cho, K.T. Lee, N.-S. Choi, Raman Spectroscopic and X-ray Diffraction Studies of Sulfur Composite Electrodes during Discharge and Charge, *Journal of The Electrochemical Society*, 159 (2012) A1308-A1314.
- [24] M.U.M. Patel, R. Demir-Cakan, M. Morcrette, J.-M. Tarascon, M. Gaberscek, R. Dominko, Li-S Battery Analyzed by UV/Vis in Operando Mode, *ChemSusChem*, 6 (2013) 1177-1181.
- [25] D.-W. Wang, Q. Zeng, G. Zhou, L. Yin, F. Li, H.-M. Cheng, I.R. Gentle, G.Q.M. Lu, Carbon-sulfur composites for Li-S batteries: status and prospects, *Journal of Materials Chemistry A*, 1 (2013) 9382-9394.
- [26] L. Xiao, Y. Cao, J. Xiao, B. Schwenzer, M.H. Engelhard, L.V. Saraf, Z. Nie, G.J. Exarhos, J. Liu, Molecular structures of polymer/sulfur composites for lithium-sulfur batteries with long cycle life, *Journal of Materials Chemistry A*, 1 (2013) 9517-9526.
- [27] M. Cuisinier, P.-E. Cabelguen, S. Evers, G. He, M. Kolbeck, A. Garsuch, T. Bolin, M. Balasubramanian, L.F. Nazar, Sulfur Speciation in Li-S Batteries Determined by Operando X-ray Absorption Spectroscopy, *The Journal of Physical Chemistry Letters*, 4 (2013) 3227-3232.
- [28] C.P. Grey, Y.J. Lee, Lithium MAS NMR studies of cathode materials for lithium-ion batteries, *Solid State Sciences*, 5 (2003) 883-894.
- [29] C.P. Grey, N. Dupré, NMR Studies of Cathode Materials for Lithium-Ion Rechargeable Batteries, *Chemical Reviews*, 104 (2004) 4493-4512.

- [30] F. Poli, J.S. Kshetrimayum, L. Monconduit, M. Letellier, New cell design for in-situ NMR studies of lithium-ion batteries, *Electrochemistry Communications*, 13 (2011) 1293-1295.
- [31] R.E. Gerald Li, C.S. Johnson, J.W. Rathke, R.J. Klingler, G. Sandí, L.G. Scanlon, ^7Li NMR study of intercalated lithium in curved carbon lattices, *Journal of Power Sources*, 89 (2000) 237-243.
- [32] R.E.G. II, J. Sanchez, C.S. Johnson, R.J. Klingler, J.W. Rathke, In situ nuclear magnetic resonance investigations of lithium ions in carbon electrode materials using a novel detector, *Journal of Physics: Condensed Matter*, 13 (2001) 8269.
- [33] B. Key, R. Bhattacharyya, M. Morcrette, V. Seznéc, J.-M. Tarascon, C.P. Grey, Real-Time NMR Investigations of Structural Changes in Silicon Electrodes for Lithium-Ion Batteries, *Journal of the American Chemical Society*, 131 (2009) 9239-9249.
- [34] Z. Rappoport, I. Marek, *The Chemistry of Organolithium Compounds*, *The Chemistry of Organolithium Compounds*, Wiley, 2004.
- [35] N.M.K. Trease, T. K.-J.; Grey, C. P., In situ NMR studies of lithium ion batteries, *Journal of the Electrochemical Society Interface*, 20 (2011) 69-73.
- [36] Y.J. Lee, F. Wang, S. Mukerjee, J. McBreen, C.P. Grey, ^6Li and ^7Li Magic-Angle Spinning Nuclear Magnetic Resonance and In Situ X-Ray Diffraction Studies of the Charging and Discharging of $\text{Li}_x\text{Mn}_2\text{O}_4$ at 4 V, *Journal of The Electrochemical Society*, 147 (2000).
- [37] J. Xiao, J. Hu, D. Wang, D. Hu, W. Xu, G.L. Graff, Z. Nie, J. Liu, J.-G. Zhang, Investigation of the rechargeability of Li-O₂ batteries in non-aqueous electrolyte, *Journal of Power Sources*, 196 (2011) 5674-5678.

- [38] L.A. Huff, J.L. Rapp, L. Zhu, A.A. Gewirth, Identifying lithium–air battery discharge products through ^6Li solid-state MAS and ^1H – ^{13}C solution NMR spectroscopy, *Journal of Power Sources*, 235 (2013) 87-94.
- [39] P.T. Callaghan, *Principles of Nuclear Magnetic Resonance Microscopy*, Clarendon Press, 1993.
- [40] P.M. Henrichs, J.M. Hewitt, R.H. Young, Baseline roll and phase distortion of NMR spectra. An algorithm for the generation of reliable powder spectra of solids, *Journal of Magnetic Resonance* (1969), 69 (1986) 460-466.
- [41] Q. Wang, S.U.o.N.Y.a.B. Chemistry, *New Materials for Chromatographic Applications*, State University of New York at Buffalo, 2007.
- [42] L.A. O'Dell, I.L. Moudrakovski, Testing the sensitivity limits of ^{33}S NMR: An ultra-wideline study of elemental sulfur, *Journal of Magnetic Resonance*, 207 (2010) 345-347.
- [43] W. Semmler, M. Schwaiger, *Molecular Imaging I*, Springer, 2008.
- [44] J. Cavanagh, W.J. Fairbrother, A.G. Palmer, N.J. Skelton, M. Rance, *Protein NMR Spectroscopy: Principles and Practice*, Elsevier Science, 2010.
- [45] Y.-S. Su, Y. Fu, T. Cochell, A. Manthiram, A strategic approach to recharging lithium-sulphur batteries for long cycle life, *Nat Commun*, 4 (2013).
- [46] S.S. Zhang, Liquid electrolyte lithium/sulfur battery: Fundamental chemistry, problems, and solutions, *Journal of Power Sources*, 231 (2013) 153-162.
- [47] T. Asakura, I. Ando, *Solid State NMR of Polymers*, Elsevier Science, 1998.